Palladium(0)-Catalyzed Synthesis of Unsaturated Polyesters from Bifunctional Vinyloxirane and Diacids

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ABSTRACT: We found that the palladium(0)-catalyzed polyaddition of a bifunctional vinyloxirane, 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**1**), with diacids gave new unsaturated polyesters having pendant hydroxyl groups in good yields. The polyaddition was carried out in THF in the presence of a Pd(0) catalyst (5 mol% for **1**). Among the diacids employed, adipic acid (**3**), fumaric acid (**5**), isophthalic acid (**7**), and terephthalic acid (**9**) could be used in the polyaddition of **1**. Maleic acid and phthalic acid did not afford the corresponding polyesters. The Pd(0)-catalyzed polyaddition with **3**, **5**, **7**, and **9** proceeded successfully when PPh₃ was used as the ligand. 1,2-Bis(diphenylphosphino)ethane (dppe) was not effective. We also found that *p*-hydroxybenzoic acid (**11**), which has a hydroxyl and carboxyl groups within the same molecule, could be used in the Pd(0)-catalyzed polyaddition of **1** and produced a new unsaturated polymer with an ether and ester moieties in the main chain. All the obtained polymers were soluble in organic solvents such as THF and dimethylsulfoxide (DMSO).

KEY WORDS Palladium(0)-Catalyzed Polymerization / Vinyloxirane / Polyaddition / Diacids / Unsaturated Polyester / Hydroxyl Group /

It is well known that unsaturated polyesters are prepared by polymerization of diols with maleic anhydride. Crosslinking of the polyesters are accomplished by radical copolymerization with vinyl monomers such as styrene. Polyesters with pendant hydroxyl groups were obtained by the polyaddition of bisoxirane derivatives with diacids. However, the polyaddition tends to afford solvent-insoluble polyesters because of crosslinking.¹ Recently, Nishikubo² and Klee³ reported that solvent-soluble polyesters with pendant hydroxyl groups could be obtained by polyaddition of bisoxirane derivatives and diacids.

Unsaturated polymers are important for synthesis of crosslinked polymers. Polymers with hydroxyl groups are also significant in reactive polymers and polymeric reagents.⁴ Therefore, unsaturated polyesters with pendant hydroxyl groups would be applicable as new reactive and functional polymers. However, it is very difficult to synthesize various such polymers by conventional methods. To our knowledge, the synthesis of unsaturated polyesters with hydroxyl groups in the side groups has not been reported. In this article, we describe the Pd(0)-catalyzed synthesis of unsaturated polyesters from 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**1**) and diacids (Scheme 1). We have recently found that the palladium(0)-catalyzed polyaddition of bifunctional vinyloxiranes [**1** and 1,4-bis(2-vinylepoxyethyl)benzene (**2**)] with nucleophiles such as active methylene compounds and bisphenol

Scheme 1. Synthesis of unsaturated polyesters from **1** and diacids.

analogues afforded various unsaturated polymers having pendant hydroxyl groups.^{5–8} Consequently, we tried the application of the Pd(0)-catalyzed polyaddition using diacids to the synthesis of unsaturated polyesters with pendant hydroxyl groups.

EXPERIMENTAL

Measurement

Fourier transfer infrared (FT-IR) spectra were measured on a JASCO FT/IR-230 spectrometer. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-DMX 500 using dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as a solvent and Me₄Si as an internal standard. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu HPLC LC-6A system equipped with two columns (Shim-pack GPC-802 and GPC-804) using tetrahydrofuran (THF) as an eluent at 45 °C. The GPC was calibrated against standard polystyrene samples.

Materials

Extra-pure grade reagents were used without further purification. Bifunctional vinyloxirane **1** was prepared by the method reported in our previous paper.⁶ THF

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Table I. Pd(0)-Catalyzed Polyaddition of **1** with Diacids (**3**, **5**, **7**, and **9**)

$\text{4: Y} = -(\text{CH}_2)_4-$ $\text{6: Y} = -\text{CH}=\text{CH}-$
 $\text{8: Y} = -\text{C}_6\text{H}_4-$ $\text{10: Y} = -\text{C}_6\text{H}_4-$

Run	Diacid (Y =)	Temp.(°C)	Time	Pd(0)	M_n^a	M_w/M_n^a	Yield (%) ^b
1	$-(\text{CH}_2)_4-$ 3	r.t.	24 h	Pd(PPh ₃) ₄	1400	2.35	92
2	3	60	6 h	Pd(PPh ₃) ₄	2800	2.29	81
3	3	r.t.	24 h	Pd ₂ (dba) ₃ /dppe ^c	—	—	0
4	$-\text{CH}=\text{CH}-$ 5	r.t.	8 d	Pd(PPh ₃) ₄	940	2.97	95
5	5	60	24 h	Pd(PPh ₃) ₄	1900	3.37	98
6	5	60	24 h	Pd ₂ (dba) ₃ /dppe ^c	—	—	0
7	$-\text{C}_6\text{H}_4-$ 7	r.t.	24 h	Pd(PPh ₃) ₄	2400	2.40	86
8	7	r.t.	24 h	Pd ₂ (dba) ₃ /dppe ^c	—	—	0
9	$-\text{C}_6\text{H}_4-$ 9	r.t.	24 h	Pd(PPh ₃) ₄	4300	2.58	99
10	9	r.t.	24 h	Pd ₂ (dba) ₃ /dppe ^c	—	—	0
11	9	60	6 h	Pd ₂ (dba) ₃ /dppe ^c	—	—	0

^aEstimated by GPC(based on PSt). ^bInsoluble in toluene. ^cPh₂PCH₂CH₂PPh₂.

used as the solvent for the Pd(0)-catalyzed polyaddition was distilled from sodium/benzophenone ketyl under nitrogen prior to use.

Pd(0)-Catalyzed Polyaddition of Bifunctional Vinyloxirane (1) with Diacids: A Typical Procedure. To a solution of Pd(PPh₃)₄ (0.058 g, 0.05 mmol) in THF (2 mL) terephthalic acid (**9**; 0.166 g, 1.0 mmol) was added. To this a solution of bifunctional vinyloxirane **1** (0.242 g, 1.0 mmol) in THF (1 mL) was added. The mixture was stirred at room temperature under an Ar atmosphere. After 24 h, the reaction mixture was poured into toluene (100 mL) to precipitate the polymer (run 9 in Table I). The resulting polymer (**10**) was filtered off, washed with toluene, and dried *in vacuo* (0.407 g, 99%) giving a yellow solid: IR (KBr): 3467, 3030, 2976, 2877, 1714, 1269, 1103, 968 cm⁻¹. ¹H NMR (DMSO-*d*₆, δ): 1.54 (CH₃, s, 3 H), 4.85 (—CH₂—, s, 4 H), 5.44 (OH, s, 2 H), 5.88–5.92 (—CH=CHCH₂—, m, 2 H), 6.17 (—CCH=CH—, d, *J* = 15.2 Hz, 1 H), 7.41 (ArH, s, 4 H), 8.08 (ArH, s, 4 H). ¹³C NMR (DMSO-*d*₆, δ): 30.3, 65.7, 72.9, 120.4, 124.9, 129.9, 134.0, 143.1, 146.1, 165.2.

Polyester **4**, a pale yellow solid: IR (KBr): 3448, 3037, 2974, 2875, 1728, 1362, 1176, 1076, 974 cm⁻¹. ¹H NMR (DMSO-*d*₆, δ): 1.49 (CH₃, s, 6 H), 1.52 (—CH₂—, s, 4 H), 2.31 (—CH₂—, s, 4 H), 4.52 (—CH₂—, d, *J* = 5.9 Hz, 4 H), 5.35 (OH, s, 2 H), 5.68–5.74 (—CH=CHCH₂—, m, 2 H), 6.01 (—CCH=CH—, d, *J* = 15.5 Hz, 2 H), 7.35 (ArH, s, 4 H). ¹³C NMR (DMSO-*d*₆, δ): 24.2, 30.0, 33.4, 64.3, 72.8, 120.6, 125.0, 142.6, 146.1, 172.9.

Polyester **6**, a pale yellow solid: IR (KBr): 3440, 3030, 2976, 2875, 1718, 1300, 1157, 976 cm⁻¹. ¹H NMR (DMSO-*d*₆, δ): 1.51 (CH₃, s, 3 H), 4.69 (CH₂, d, *J* = 4.4 Hz, 4 H), 5.39 (OH, s, 2 H), 5.77–5.81

(—CH=CHCH₂—, m, 2 H), 6.10 (—CCH=CH—, d, *J* = 15.4 Hz, 2 H), 6.80 (—CH=CH—, s, 2 H), 7.38 (ArH, s, 4 H). ¹³C NMR (DMSO-*d*₆, δ): 30.0, 65.5, 72.8, 120.0, 125.0, 133.6, 143.2, 146.1, 164.4.

Polyester **8**, a white solid: IR (KBr): 3442, 3030, 2974, 2877, 1722, 1232, 1074, 966 cm⁻¹. ¹H NMR (DMSO-*d*₆, δ): 1.54 (CH₃, s, 6 H), 4.85 (—CH₂—, d, *J* = 5.2 Hz, 4 H), 5.43 (OH, s, 2 H), 5.87–5.92 (—CH=CHCH₂—, m, 2 H), 6.17 (—CCH=CH—, d, *J* = 15.4 Hz, 2 H), 7.41 (ArH, s, 4 H), 7.65–7.68 (ArH, m, 1 H), 8.20 (ArH, d, *J* = 7.6 Hz, 2 H), 8.48 (ArH, s, 1 H). ¹³C NMR (DMSO-*d*₆, δ): 30.0, 65.7, 72.9, 120.4, 125.1, 128.5, 130.2, 131.0, 134.0, 143.2, 146.1, 165.0.

Polymer **12**, a pale yellow solid: IR (KBr): 3427, 3032, 2976, 2931, 2871, 1703, 1604, 1254, 1169, 1105, 972 cm⁻¹. ¹H NMR (DMSO-*d*₆, δ): 1.56 (CH₃, s, 6 H), 4.66 (—CH₂—, s, 2 H), 4.80 (—CH₂—, s, 2 H), 5.42 (OH, s, 2 H), 5.88–5.91 (—CH=CHCH₂—, m, 2 H), 6.13–6.18 (—CCH=CH—, m, 2 H), 7.07 (ArH, d, *J* = 7.8 Hz, 2 H), 7.41 (ArH, s, 4 H), 7.94 (ArH, d, *J* = 8.1 Hz, 2 H). ¹³C NMR (DMSO-*d*₆, δ): 30.0, 67.4, 68.5, 72.9, 115.1, 120.9, 122.3, 125.1, 131.6, 142.6, 146.2, 162.6, 165.5.

RESULTS AND DISCUSSION

First, the Pd(0)-catalyzed polyaddition of bifunctional vinyloxirane **1** with adipic acid (**3**) and fumaric acid (**5**) was carried out in THF under an Ar atmosphere. The resulting polymers were isolated by pouring the reaction mixture into toluene. The results are summarized in Table I. When Pd₂(dba)₃·CHCl₃ (where dba is dibenzylideneacetone)/1,2-bis(diphenylphosphino)ethane (dppe) was used as a catalyst, the corresponding polymers from **3** and **5** were not obtained (runs 3 and 6). On the other hand, the polyaddi-

Table II. Pd(0)-Catalyzed Polyaddition of **1** with *p*-Hydroxybenzoic Acid (**11**)

Run	Pd(0)	Temp.(°C)	Time(h)	M_n^a	M_w/M_n^a	Yield (%) ^b
1	Pd(PPh ₃) ₄	r.t.	24	2700	1.76	100
2	Pd(PPh ₃) ₄	60	6	3200	2.11	100
3	Pd ₂ (dba) ₃ /dppe ^c	r.t.	24	—	—	0
4	Pd ₂ (dba) ₃ /dppe ^c	60	6	3900	2.27	96

^aEstimated by GPC(based on PST). ^bInsoluble in toluene. ^cPh₂PCH₂CH₂PPh₂.

tion using Pd(PPh₃)₄ gave the desired polymers in good yields.⁹ The polyaddition of **1** and **3** afforded the unsaturated polyester (**4**) in a 92% yield [number-average molecular weight (M_n) = 1400; run 1]. Polyester **4** with a higher M_n value was obtained by polymerization at 60 °C for 6 h (M_n = 2800; run 2). Vinylloxirane **1** did not react with **3** in the absence of Pd(PPh₃)₄ under the same conditions. The M_n values of polyester **6** obtained from fumaric acid (**5**) were lower than those of **4** (runs 4 and 5). The polyaddition of **1** and **5** was carried out in THF at room temperature for 8 d and gave the desired product **6**. However, the M_n value was low (M_n = 940). The M_n value of the obtained polyester **6** was 1900, after polymerization even at the elevated temperature (60 °C) for 24 h. Thus, the Pd(0)-catalyzed polyaddition of **1** proceeded more effectively when adipic acid was employed. The polyaddition of **1** was also examined using maleic acid instead of **5**, but the corresponding polyester was not obtained. In addition, although the polyaddition of **3** and **5** was performed by use of 1,4-bis(2-vinylepoxyethyl)benzene (**2**) under various conditions, the desired polyesters were not produced, probably due to β -hydrogen elimination of the π -allylpalladium intermediate generated by oxidative addition of Pd(0) to **2**.^{5,6}

The structures of polyesters **4** and **6** were determined on the basis of the IR and NMR spectra. The methylene protons (—CH₂—O—) of **4** and **6** were observed at 4.52 and 4.69 ppm, respectively. In addition, signals due to the vinyl proton (—CCH=CH—) of **4** and **6** appeared at 6.01 and 6.10 ppm, respectively. The observation of these protons reveals that the polyaddition proceeded accompanying carbon-oxygen bond cleavage of the oxirane ring. The stereochemistries of **4** and **6** were confirmed as *E* configurations by the coupling constant of the vinyl proton (—CCH=CH—); the *J* values of **4** and **6** were 15.5 and 15.4 Hz, respectively. The *Z*-isomers were detected neither in the ¹³C NMR spectra nor in the ¹H NMR spectra of **4** and **6**, similarly to the polyaddition of **1** and carbon nucleophiles.^{5,6} The IR spectra of **4** and **6** showed the characteristic absorptions based on the hydroxyl groups around 3450 and 3440 cm⁻¹, respectively. Furthermore, the ester groups of **4** and

6 were observed around 1730 and 1720 cm⁻¹, respectively. From these NMR and IR spectral data, we confirmed that the Pd(0)-catalyzed polyaddition of **1** with **3** and **5** produced the desired unsaturated polyesters with pendant hydroxyl groups.

Second, we examined the Pd(0)-catalyzed polyaddition of **1** using aromatic diacids [phthalic acid, isophthalic acid (**7**), and terephthalic acid (**9**)]. Among the aromatic diacids employed, phthalic acid did not give the corresponding polyester. Neither phthalic acid nor maleic acid was suitable for the polyaddition with **1**. The polyaddition of **1** with **7** and **9** was carried out in THF at room temperature for 24 h. When dppe was used as a phosphine ligand, the desired polyesters were not obtained (runs 8 and 10). On the other hand, PPh₃ gave the corresponding polyesters in good yields. In the polyaddition of **1** with **7**, polyester **8** was formed in an 86% yield (M_n = 2400; run 7). The M_n value of the obtained polymer **10** from **9** was higher than that of **8** (M_n = 4300; run 9). Thus, the Pd(0)-catalyzed polyaddition of **1** proceeded more effectively when **9** was employed. The polyaddition with phthalic acid, **7**, and **9** was largely affected by the position (*o*-, *m*-, and *p*-) of two carboxyl groups on the benzene ring; the M_n values and yields of the polymers increased in the following order: phthalic acid (*o*-) << **7** (*m*-) < **9** (*p*-).

Finally, the Pd(0)-catalyzed polyaddition of **1** was examined by use of *p*-hydroxybenzoic acid (**11**). Table II shows the results. In the polyaddition at room temperature for 24 h with Pd(PPh₃)₄, the desired polymer **12** was obtained quantitatively (M_n = 2700; run 1). The M_n value of **12** obtained by polymerization at 60 °C for 6 h was somewhat higher (M_n = 3200; run 2). The polyaddition at room temperature using Pd₂(dba)₃ · CHCl₃/dppe as a catalyst did not afford polymer **12** (run 3), whereas the polyaddition at the elevated temperature (60 °C) proceeded efficiently and gave the desired polymer **12** in a 96% yield (M_n = 3900; run 4), contrary to the polyaddition with **9** (run 11 in Table I). The structure of **12** was confirmed with IR and NMR spectra. A new type of unsaturated polymer **12** having an ether and ester moieties in the main chain could be obtained by the Pd(0)-catalyzed polyaddition of **1** with

11 having a hydroxyl and carboxyl groups. This fact indicates that the Pd(0)-catalyzed polyaddition with **1** is a useful method for the synthesis of unsaturated polymers having different functional groups in the main chain.

CONCLUSION

We found that the Pd(0)-catalyzed polyaddition of bifunctional vinyloxirane **1** and diacids (**3**, **5**, **7**, and **9**) gave unsaturated polyesters with pendant hydroxyl groups. All of the obtained polyesters were soluble in organic solvents such as dimethylsulfoxide (DMSO) and THF. In addition, we found that nucleophile **11**, which has a hydroxyl and carboxyl groups within the same molecule, could be used in the Pd(0)-catalyzed polyaddition of **1** to synthesize a new unsaturated polymer with an ether and ester moieties in the main chain.

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